FLEXICOKE APPLICATIONS IN THE VENEZUELAN STEEL MAKING INDUSTRY

Druso Esteller SIDOR (Centro de Investigación). Matanzas, Edo. Bolívar, Venezuela
María Specht INTEVEP, S.A. Apdo. 76343, Caracas, Venezuela

INTRODUCTION:

In 1983 the oil refinery of LAGOVEN in Amuay installed a noncatallytic conversion process of heavy feedstock called Flexicoking. The plant has been in operation for seven years producing a by product known as flexicoke, at an aproximate rate of 300 metric tons per day. As a result, aproximate 400 thousand metric tons of solid are currently stored, posing serious problems of solids waste disposal. The flexicoke has a high carbon content, low volatile material and high heating value which makes it attractive for metallurgical applications. In 1987 a research group conformed by SIDOR (Venezuelan Steel Making Plant), INTEVEP (Venezuelan oil research institute) and LAGOVEN started activities oriented to investigate the different possibilites of flexicoke metallurgical applications. Among the possibilities studied were: flexicoke as pyroconsolidating agent, (added during pelletizing) and as foaming slag promoter for steel electric arc furnaces. The work reported here has been performed at laboratory, pilot plant and industrial scales. The laboratory work dealt with the characterization of the flexicoke. The pilot plant work dealt with the production of iron ore pellets using flexicoke as an addietive to improve the pyroconsolidating process and the mechanical behaviour of the iron oxide pellets. And the industrial work dealt with the evaluation of flexicoke as a foaming slag promoter.

EXPERIMENTAL PROCEDURE:

The experimental procedure followed in this work is shown esquematically in Fig. 1. The main characteristics of the flexicoke used in this work is shown in Table 1. If this material is compared with the metallurgical coke, used by SIDOR (see Table same) it can be observed that the main difference is the sulphur content which may impose limitations to flexicoke applications in the steel making industry. The main objective of the investigation was to determine up to which level flexicoke could substitute metallurgical coke.

Besides the chemical and physical analysis of the flexicoke given in Table 1, a morphological characterization and element distribution was performed by using scanning and transmision mycroscope analysis in order to have a better understanding of flexicoke behaviour in these particular metallurgical applications.

In order to evaluate flexicoke as pyroconsolidating agent, the procedure shown schematically in figure 2 was followed. The chemical analysis of the iron ore, dolomite, hydrated lime and sand used are indicated in Table 2.

The mixture patterns are given in Table 3. It was added 8% of water to the mixture and pelletized in a 120 cm diameter disc at 14 rpm, this configuration has a pellet production of 60 kg/h. During pelletizing more water was added up to achieve 10% in the pellet. The compresion strength and drop resistance were the two parameters evaluated in the product obtained (ie, green pellet). The drop resistance test consists of register the number of times a pellet drops from 46 cm height before it presents cracks. The reported value is often the mean value among 10 pellets. The compression strenght, also called crushing strength is the force applied on a pellet up to it breaks, it is generally reported as kg/pellet.

The pellets were burnt in a pot grate. The temperature ranged between 1260°C and 1320°C; for 30 to 45 minutes. The parameters considered for the burnt pellets evaluation were compression strength, porosity, drum abrasion index and pellet reducibility. The criteria of acceptance or rejection of these pellets were the same considered by SIDOR for their conventional iron oxide pellets (ie, with no carbon addition). The reducibility tests were performed in a vertical reactor when 500 g of burnt pellets were heated up to 850°C in a N_2 atmosphere. When achieved this temperature a reducing atmosphere composed of CO, CO_2, H_2, H_2O was run for 90 minutes. During this period the loss weight fraction was recorded to calculate the metallization percentage according to the following equation:

% Met = (iron mass/total iron mass as obtained by chemical analysis) x 100.

The drum abrasion index was determined by reducing 500 g of burnt pellets at 550°C for 2 h in a rotary tubular furnace (Linder type). The heating up and cooling down of the sample was performed with a flow of N_2. The cold reduced sample was screened and the percentage < 6,35 mm was taken as the drum index, according to SIDOR, this must be less than 10%.

For the evaluation of flexicoke as foaming slag promoter the procedure shown in figure 3.

The slag in the steel making electric arc furnace has not only the function of trapping steel impurities but also as thermal barrier. The heat introduced inside the furnace is from tipically three carbon electrodes arc, where temperatures higher than 3500°C are generated. This is much higher than the melting point of the furnace refractory linning. Therefore, after the furnace metallic charge is melted, the furnace sidewalls are exposed to this intense radiation except for the portion of the arc that can be submerge below the slag cover that is created on top of the molten metal. The common practice is to add CaO not only for sulphur and phosphorous removal, but for covering the arc as much as possible.

In order to increase SIDOR electric arc furnace operability and decrease refractory consumptions refrigerated panels were installed on the outside walls of the furnaces, this modification implies the use of a foaming slag promoter. When carbonaceous materials such as graphite, metallurgical coke, lignite coke, etc, react with the ferrous oxide contained in the slag, CO gas in generated, the entrapped CO bubbles tend to increase the slag volume, covering in this manner the electric arc and dissipating the heat radiation that erode the refractory linning.

Previously, SIDOR tested fine metallurgical coke (mean particle size aproximately 1 mm) by injecting it through the system showed schematically in figure 4 but the usage of this material implied high consumption of valves, hoses and conexions due to its high abrasivity. Taking this into consideration, it was decided to test with flexicoke. The parameters considered during the evaluation were: operability of the injection and remnant sulphur content in the steels, since flexicoke has a sulphur content of 2,6% (62% higher than metallurgical coke).

120 metric tons of flexicoke were charged to a silo of 150 tons capacity through an air pneumatic system, at a pressure of 6 kg/cm² by a hose and pipe of 101,6 mm diameter. The flexicoke was injected on the incipient slag already formed in the electric arc furnace due to the melting of the initial metallic charge. Two electric arc furnaces were used one of 150 tons of steel capacity, where carbon steels for bars are produced, here the maximum sulphur content in the steel is 0,030%. The other, was 200 tons of steel capacity where carbon steels for slabs are produced, here is programed the production of steels with maximum sulphur content of 0,010%; 0,015% and 0,025%. Aproximately 1 or 2 tons of flexicoke per steel heat where injected. A total of 85 steel heats were evaluated.

RESULTS AND DISCUSSION

CHARACTERIZATION OF FLEXICOKE:

The flexicoke is formed during thermal cracking of the heavy residues. The break down of the large hydrocarbon molecules occurs at the surface of the heated solid particles (seed). As a result, light hydrocarbons are produced and the seeds grow in size due to the continous deposition of carbon, sulphur and metallic compounds: vanadium and nickel. A fraction of these particles stay within the reactor and the heater of the flexicoking unit, exiting the process at the elutriator when they reach an approximate mean size of 100 microns. This fraction constitute the bed coke particles and represents 80% of the total flexicoke production, their typical shape is shown in figure 4 as, can be seen, they are rounded with smaller protuberances on their surface. The inner structure of the bed coke is shown in figure 4b where also can be observed, the metals and sulphur distribution in the particle. Notice the onion like structure produced by continuous deposition of heavy, inorganic and organic substances on the solid substrate during the reactor-heater, heater-reactor cycle. Also, it can be observed that sulphur and nickel are homogeneously distributed in the particle, while vanadium tends to concentrate in the inner of the particle. The sulphur is present as organic compound as it is revealed by the transmission electron micrograph in figure 5.

FLEXICOKE AS PYROCONSOLIDATING AGENT:

Table 3 summarizes the results obtained when using flexicoke as an additive in the manufacture of iron oxide pellets. Here, it can be observed that pellets mechanical properties have increased with the addition of flexicoke up to 1%. After it, the mechanical properties decrease abruptly.

Figure 6 (a) and (b) show that the production rate and the productivity of the pelletizing process increases with additions of flexicoke up to 1%. SIDOR plans to increase the pellet plant production from 6,6 million tons/year up to 8,0 million tons/year. Flexicoke additions to pellets manufacturing would help to increase the productivity of this plant with minor equipment modifications, that would represent the instalation of a flexicoke feeder. This represents to SIDOR a consumption of 80 thousand tons/year of flexicoke.

FLEXICOKE AS FOAMING SLAG PROMOTER:

The operability of the injection system was 100%, after being used 120 tons of flexicoke, a visual inspection of the valves, hoses and conexions revealed no erosion of the internal parts.

The flexicoke was injected during the fusion period, parallel to reduced sponge iron feeding. The optimum rate of injection was 30-40 kg/min. With this value the "swelling" of the slag was continuous improving furnace operation and decreasing noise level. At higher flexicoke injection rates, explosion between the electrodes and incontrolable flames were observed that led to decrease the furnaces between working power and the feeding rate of sponge iron.

With respect to the sulphur and carbon transference from the slag to the molten steel due to flexicoke injection; it was found that in the 150 tons capacity steel making electric arc furnace, 30% of the heats evaluated, the sulphur increments were from 0.001 up to 0.007%. The distribution of these sulphur increments in the steel heats are indicated in figure 7. In the 70% of the heats no sulphur increments were detected, on the contrary, it tend to decrease due to the simultaneous addition of CaO.

The carbon content was also evaluated, but in the 92% of the heat, no increments were detected, mainly because the flexicoke injection was on the incipient slag and flexicoke low density and high reactivity did not allow to get into the molten steel.

In the 200 tons steel capacity electric arc furnace, 66% of the heat evaluated showed increments from 0.002 up to 0.008 of sulphur. The distribution of these sulphur increments are indicated in figure 1, where it can be observed that 61% of the heats showed sulphur increments less than 0.004%. Since in this furnace, steels with more sulphur restrictions are produced, it was recomended to inject flexicoke for steels with maximum sulphur content of 0.025%. For those steels with maximum sulphur content of 0.015% the injection of flexicoke should be only during first stage of fusion period. And for those steels with maximum sulphur content of 0.010% not to use flexicoke as foaming slag promoter.

The potential consumption of flexicoke for this particular application in SIDOR is 31 thousand tons/year (11 thousand tons for 20 tons steel capacity electric arc furnace and 20 thousand tons for the 150 tons steel capacity furnace).

Only in this two applications 121 thousand tons of flexicoke per year has to be handled and transport through 18000 km distance from LAGOVEN Amuay to SIDOR through marine transportation. Although there is proven technical feasibility of using flexicoke in the steel making industry. The transportation of high tonage of this material with 100 micros mean particle size is critical, due to powder emissions to the atmosphere. The handling and transportation involves pneumatic systems increasing its costs. The evaluation of agglomerate flexicoke in briquettes is considering now in order to diminuish transportation costs and reduce environment impact. These results will be published later on.

CONCLUSIONS:

Flexicoke can be used in the venezuelan steel making industry as pyroconsolidating agent for iron oxide pellet manufacturing, improving its mechanical strength, level of porosity and reducibility when added up to 1%. The pellet plant production and productivity is also increased with flexicoke additions.

Flexicoke can be used as foaming slag promoter in the steel making electric arc furnace, but its sulphur content restricts its application to steel production of 0.025% - 0.030% S maximum.

Flexicoke can partially substitute metallurgical coke in these particular applications. But the handling and transportation of this material with such a fine particle size remains a critical point.

RECOMENDATION:

An economical study must be perfomed in order to evaluate the investment costs for handling and transportation of flexicoke in its original particle size and if it comparable to metallurgical coke price in powder form. Also the option of agglomerating flexicoke in briquettes must be considered from technical and economical point of view.

Table 1. Characteristics of flexicoke and metallurgical coke (traditionally used by SIDOR).

Analysis	Flexicoke (Bed coke)	Metallurgical coke
%C	91,7	88,0
%S	2,6	<1,0
%V	1,58	-
%N	0,36	-
Volatile material	2,6	<3,0
Ash	3,3	40
Density	1,89	-
Heating value (cal/g)	7305	7337
Mean particle size	100 microns	>3mm

Table 2. Chemical analysis of iron ore, binders and other additives.

Analysis (w%)	Iron ore	Dolomite	Hydrated lime	Sand
Fe_{tot}	66,21	2,11	2,13	0,728
SiO_2	1,34	4,30	1,53	95
CaO	0,03	31,96	63,68	0,61
MgO	0,02	15,44	2,83	0,11
Al_2O_3	0,51	0,33	0,32	1,46
P	0,035	-	-	-
S	-	-	-	-

Table 3. Mixture patterns (weight %).

Flexicoke	Iron ore	Dolomite	Hydroted lime	Saud
0	94,96	2,72	1,89	0,73
0,5	94,51	2,84	1,89	0,76
1,0	96,51	2,84	1,89	0,76
1,5	94,51	2,84	1,89	0,76
2,0	94,51	2,84	1,89	0,76

Table 4. Summary of the results obtained when using flexicoke as an additive for iron oxide pellet production.

% Flexicoke	Green pellets	Burnt pellets				
	Crushing strength (kg/pellet)	Crushing Strength (kg/pellet)	Abrasion Index	Drum Index	Porosity	Reducibility $K(10^{-2}/min)$
0	2.45	221	5.26	91.20	15.2	2.6
0.5	1.97	321.3	4.78	93.10	20.49	2.85
1.0	1.80	375.0	4.75	93.54	19.43	3.25
1.5	2.27	144.67	5.19	92.31	-	-
2.0	2.6	100.5	5.49	87.96	-	-

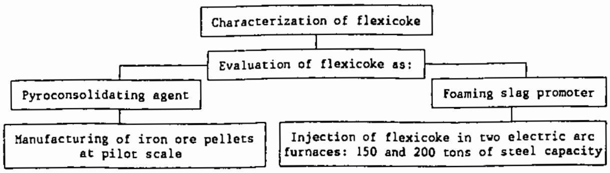

Fig. 1. Experimental procedure.

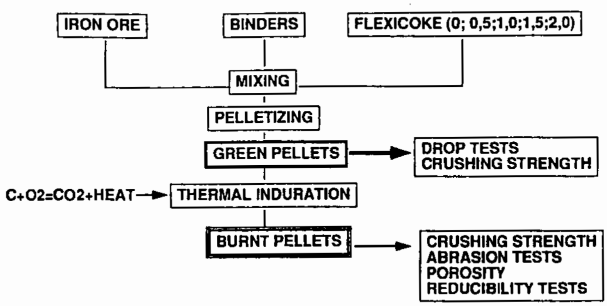

Fig. 2. Procedure followed for manufacturing iron ore pellets with flexicoke as pyroconsolidating agent.

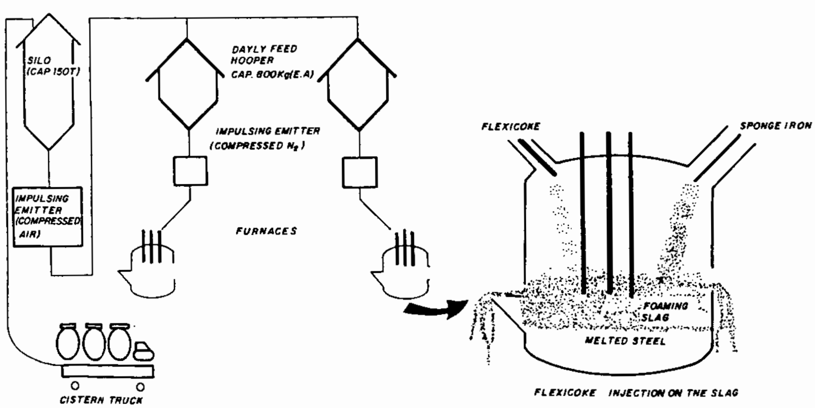

Fig. 3. Procedure for evaluation of flexicoke as foaming slag promoter.

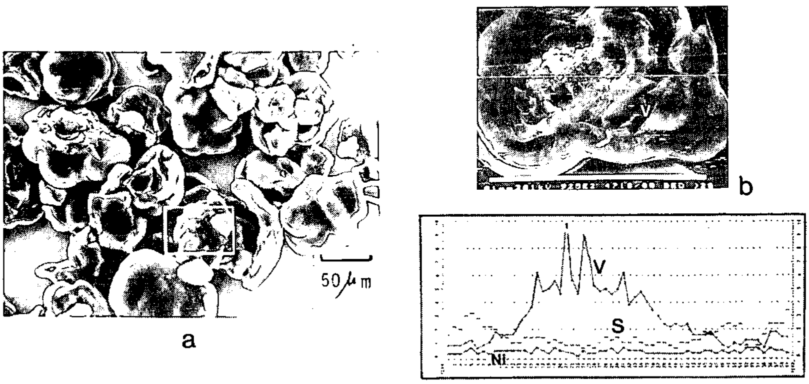

Fig. 4. (a) Scanning photomicrograph of flexicoke (bed coke). (b) V, Ni and S profile. On the photomicrograph the vanadium concentration profile is superimposed.

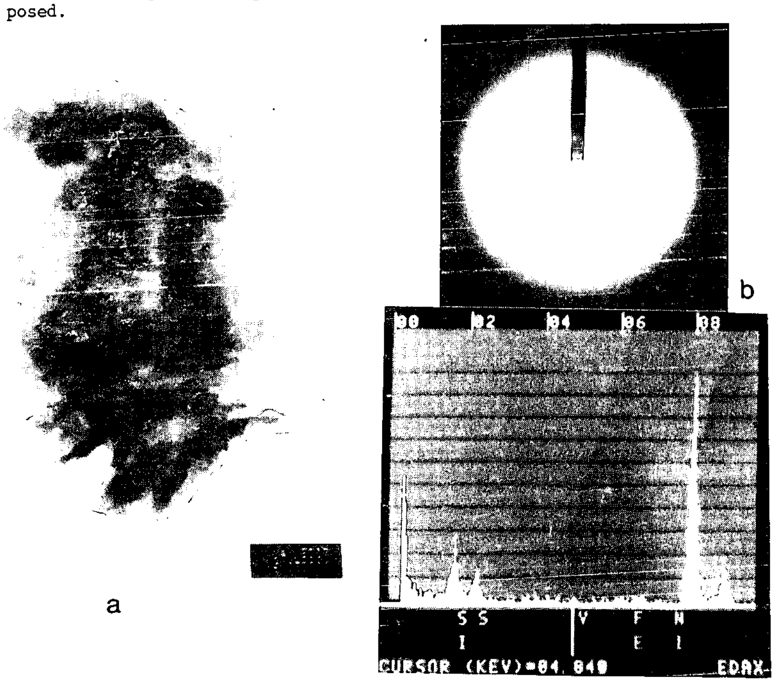

Fig. 5. Transmision photomicrograph of a bed coke particle (a). Difraction pattern of the organic sulphur compound (b).

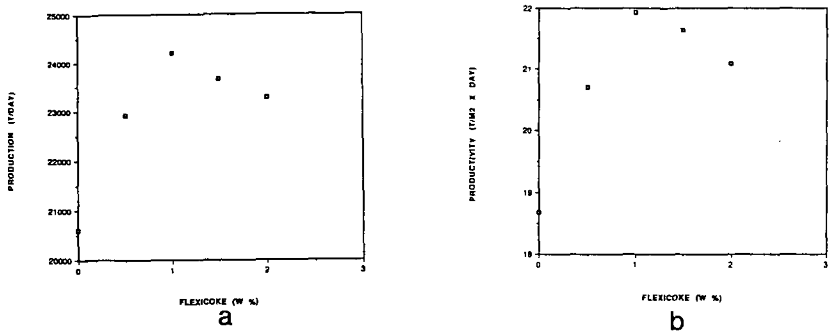

Fig. 6. (a) Production behaviour with flexicoke additions (b) Productivity.

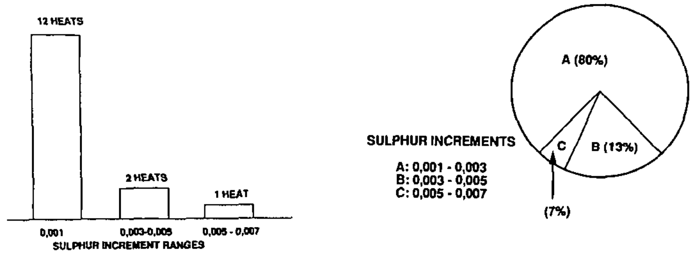

Fig. 7. Distribution of sulphur increments in the evaluated steel heats produced in the electric arc furnace 150 tons of steel capacity.

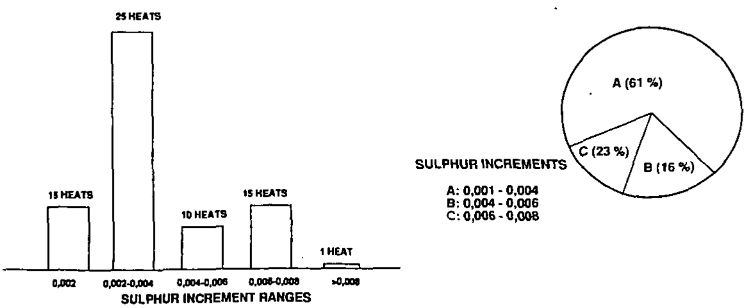

Fig. 8. Distribution of sulphur increments in the evaluated steel heats produced in the electric arc furnace 200 tons of steel capacity.